SCIENCE FOR CERAMIC PRODUCTION

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CONTROLLING PROPERTIES OF MOLDING MIXTURES BASED ON TECHNICAL ALUMINA

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The effect of the quantity of paraffin and the method of its introduction into a molding mixture (after dispersion or in joint dispersion) prepared from technical alumina and 20% nitric acid is studied. It is established that mechanochemical activation in the presence of paraffin makes it possible to achieve a greater effect in controlling structural-mechanical and flow properties. The factors responsible for the properties of molding mixtures are considered.

The traditional technology for preparing extruded catalyst carriers for high-temperature processes based on technical alumina (for instance, grades GIAP-3, GIAP-8, etc.) is based on peptization of initial material ground in a mill using a solution of 20% nitric acid [1]. Molding mixtures produced by the above method have predominantly slow elastic deformations and belong to the first structural-mechanical type. Furthermore, these mixtures have a relaxation period of about 26,000 – 28,000 sec. Such combination of parameters in a molding mixtures prevents using it to mold cellular blocks, as its plastic deformations are not sufficiently developed and the relaxation period more than 10 times exceeds the optimum value [2, 3].

The replacement of nitric acid by a surfactant – water system used as a dispersion medium does not ensure properties needed for extruding blocks of a cellular structure either, since in this case the required values of coagulation structure strength and flow index are not achieved. Extrusion is hampered as well by considerable adhesion of molding mixture to the die material, which ought to be minimum [4].

A method for improving molding properties was proposed in [5] in the form of joint dispersion of the solid phase, in particular, alumina together with surfactant additives. The effect of surfactant additives on mechanical-chemical activation (MCA) of alumina was investigated in [6], where the main attention was paid to the effect of PVA additive on the process of MCA of alumina. It was noted that a paraffin additive at the stage of dispersion has approximately the same effect on the alumina substructure parameters.

The purpose of our study was to investigate the relationship between variations of the parameters of alumina milled in the presence of paraffin and without it and the structural-mechanical and flow properties of molding mixtures based on this alumina using the nitric-acid technology.

The initial materials were technical alumina G-00, technical paraffin T-2, and 20% nitric acid.

Alumina in the presence of paraffin or without it (in that case paraffin was added at the subsequent stage) was subjected to MCA in a roll-ring vibration mill VM-4 (vibration frequency 930 $\min^{-1}$, power intensity 5.4 kW/kg). After activation the solid phase was mixed with an estimated quantity of nitric acid to obtain a homogeneous mixture of moisture 19 – 20%, which is the optimum molding moisture [5], which was monitored using a conic plastometer designed by P. A. Rebinder [7].

The structural-mechanical properties of molding mixtures were calculated on the basis of the flow curves obtained on a plastometer designed by D. M. Tolstoi processed using the Maxwell – Shvedov and Kelvin equations [7].

The flow properties were determined using the total flow curves obtained on a Rheotest-2 rotation viscometer. The total power in a flow and the power expended for destroying the coagulation structure was calculated by integrating the rheological curves in the shear velocity – shear stress coordinates. The consistency constants η_0 and the flow index n were found using the Ostwald equation [2]:

$$\eta = \eta_0 |v|^{n-1},$$

where η is the effective viscosity, Pa · sec and v is the shear velocity, $\sec^{-1}$.

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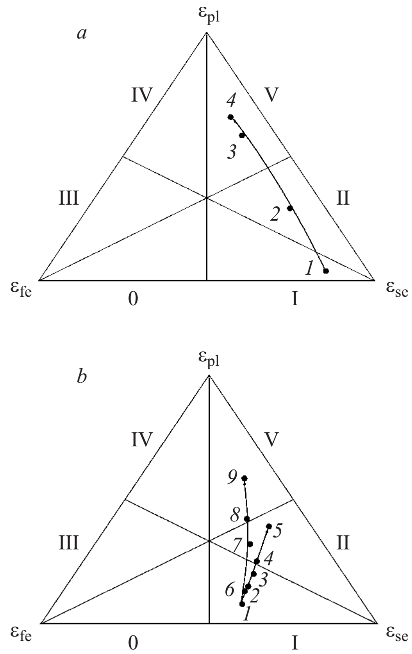

Fig. 1. Diagram of evolving deformations in molding mixtures based on alumina (mechanically activated) – paraffin – nitric acid (*a*) and alumina – 5% paraffin – nitric acid (*b*) systems. Deformation (100%): ε_{fe}) fast elastic, ε_{se}) slow elastic, ε_{pl}) plastic; *a*: *1*) without paraffin, *2*, *3*, and *4*) 3, 5 and 7% paraffin, respectively, *b*: *1*) without MCA, *2*, *6*) MCA for 15 min, *3*, *7*) the same, 30 min, *4*, *8*) 45 min, *5*, *9*) 60 min, *2* – *5*) activated without paraffin, *6* – *9*) activation in the presence of paraffin.

The mean quadratic value of microdeformations was calculated based on x-ray-structural analysis data according to recommendations in [8]. The mean radius of particles and the coordination number in the polydisperse system were determined based on sedimentation analysis data [9].

It was demonstrated in [6] that the quantity of a surfactant[2] at the stage of MCA (both PVA and paraffin) does not have a significant effect on substructural parameters of alumina. At the same time, the molding properties of mixtures are very sensitive to them [5, 7]. Therefore, at the first stage of research we identified the optimum content of paraffin to introduce into the molding mixture. It was found (Fig. 1*a*) that as the content of paraffin increases, the share of plastic deformations after MCA of alumina for 60 min becomes significantly higher. The share of fast elastic deformation remains at the same level (10 – 12%) and the slow elastic deformations decrease virtually to one-fourth. It should be noted that the most significant improvement of plastic properties is registered with a paraffin content up to 5%. Thus, the additive of 3% paraffin makes it possible to convert a mixture from the first structural-mechanical type to the second type, and a 5% additive — to the fifth type with prevailing plastic deformations. A further increase in the content of paraffin in the molding mixture to 7% leads to a slight increase in the share of plastic deformations, which is undesirable [2]. Thus, the optimum content of paraffin in a molding mixture is 5%, since precisely such combination of all types of deformations is needed for extruding blocks with a cellular structure [2, 3].

A powerful method for controlling properties of molding mixtures is the introduction of a surfactant additive and increasing the duration of MCA.

It can be seen from Fig. 1*b* that as the duration of MCA of alumina in a vibration mill increases, the plastic properties improve regardless of the method of introducing paraffin into the mixture, which is manifested in a higher share of plastic deformations. In this case the share of fast elastic deformations decreases to more than one-third and the share of slow elastic deformations drops from 56 to 48% (dispersion without surfactancts) and to 31% (dispersion in the presence of paraffin). Note that whereas in the case of MCA of alumina without surfactants, the increase in the share of plastic deformations proceeds monotonically with increasing dispersion duration, MCA in the presence of paraffin produces a substantial jump within 15 – 30 min. However, on further increase in the duration of alumina activation in the presence of paraffin, the growth in the share of plastic deformations remains significant.

Figure 2 shows the dependences of the structural-mechanical constants of molding mixtures on duration of alumina MCA. It can be seen that with increasing activation duration, we observe growth in the elasticity modulus E_1 and shear modulus E_2 as well as shear stress P_{k1}. Mechanical treatment of alumina in the presence of paraffin yields higher values of these constants. It should be noted that molding mixtures prepared from alumina activated without surfactants typically display a rather monotonic increase of these parameters for dependences of E_1, E_2, and P_{k1} on MCA duration in the entire range considered. Activation of alumina in the presence of paraffin changes the situation. During 15 – 45 min a sufficiently sharp increase in the specified constants is registered. A further treatment of alumina in the mill does not change significantly the values of E_1, E_2, and P_{k1}.

The maximum plastic viscosity decreases with increasing activation duration (Fig. 2*b*). At the same time, the values η_1 in samples dispersed in the presence of paraffin are slightly lower. Note as well that alumina activation without a surfactant produces a virtually linear decrease in viscosity, whereas in MCA for over 45 min in the presence of paraffin the value η_1 changes little.

The above described behavior of the structural-mechanical constants leads to increased plasticity of the system and a decreased relaxation period, whereas the elasticity remains at

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[2] In this case, according to P. A. Rebinder, a surfactant is understood as any compound modifying the surface energy. As for the particular Al_2O_3 – paraffin system, it should be noted that the surface of aluminum oxide has both lyophilic and lyophobic properties, i.e., certain sites of the surface of Al_2O_3 particles have affinity to lyophobic molecules of paraffin. Moreover, in joint MCA of alumina and paraffin, mechanical cracking of the latter is observed, which also contributes to adsorption of radicals formed on the surface of alumina particles.

approximately the same level (Table 1). The growth in plasticity in samples prepared using joint MCA of alumina and paraffin is 1.5 times higher. The relaxation period in the specified samples as well decreases more intensely than in the case of activating the solid phase without the surfactant (decrease more than 10 times and 3 times, respectively).

The MCA of alumina substantially increases the strength of the coagulation structure, which is evidence by the increased power expended for its destruction. Furthermore, the flow index of molding mixtures decreases as well. In this case the main growth in strength of the coagulation structure and decrease in the flow index are registered in the first 15 min of MCA.

After 15 min of dispersion, the particle size does not change, nor do the size of the coherent scattering area and the specific surface area of Al_2O_3 change [6]. However, an increase in duration of MCA of alumina particles increases the amount of defects in its particles, which is manifested in increased mean quadratic microdeformations. Activation in the presence of paraffin produces substantial distortions in the crystal lattice. Thus, the value of microdeformation after 60 min of dispersion without surfactants grows from 0.18 to 0.42%, whereas the use of paraffin at the dispersion stage makes it possible to achieve deformation of 0.84%.

It is known [10] that chemical activity of the solid phase grows with increasing amount of its defects. This is due to the fact that defective areas of the surface have excessive energy, and, accordingly, all interactions with this particular surface (for instance, adsorption, chemical reactions) will primarily occur on these areas, and the higher the excessive energy, the higher the probability of reactions. In our case the growth in chemical activity is corroborated by an increased degree of dissolution of alumina in 20% nitric acid (Table 1), where the higher microdeformations, the greater the chemical activity of the solid phase.

The higher chemical activity of alumina at the stage of preparation of a molding mixture and formation of its structure with a substantial (80 – 81%) content of the disperse phase produces the following results. First, the quantity of aluminum hydroxonitrate formed on the surface of particles as a consequence of peptization grows [5]. Second, the sorption capacity of alumina with respect to paraffin molecules grows as well. Thus, the number of links capable of forming coagulation contacts between the solid phase particle increases.

The above is corroborated by a change in the structural-mechanical constants. The elasticity modulus and the shear modulus of moldings mixtures increase (Fig. 2*a*). This means that, according to Hooke's law, a higher external stress is needed for the development of an elastic deformation of equal relative value, which is a result of the modification of the nature of coagulation interaction in the disperse system. The shear stress values grow as well (Fig. 2*b*). This shows that a stronger external impact is needed for initial destruction of coagulation contacts and for plastic (i.e., irreversible) deformation. Strengthening of coagulation bonds is

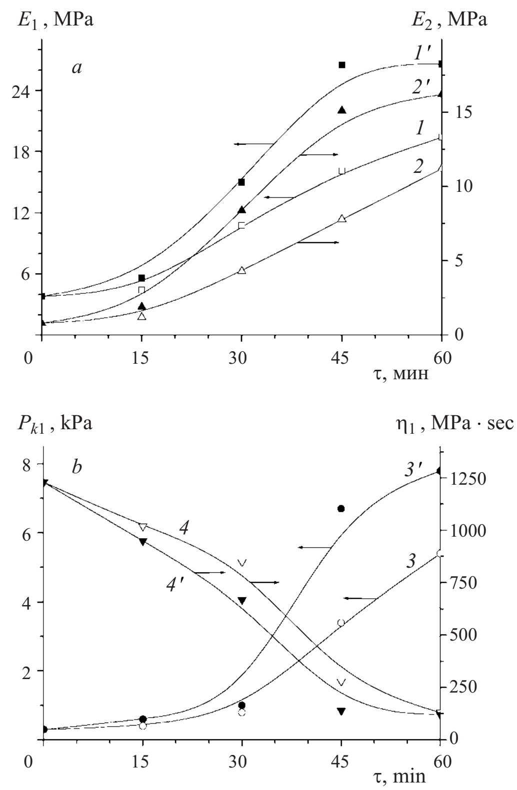

Fig. 2. Dependence of structural-mechanical constants of molding mixtures based on alumina – 5% paraffin – nitric acid system on duration τ of MCA of alumina: *1*, *1′*) elasticity modulus E_1; *2*, *2′*) shear modulus E_2; *3*, *3′*) shear stress P_{k1}; *4*, *4′*) maximum plastic viscosity η_1; *1* – *4*) MCA without surfactant; *1′* – *4′*) the same in the presence of 5% paraffin.

confirmed by the growth in power expended for destroying the coagulation structure (Table 1). A higher content of the binder in the system ensures increased fluidity of the mixture (with stress $P \geq P_{k1}$), which is indicated by a decrease in the maximum plastic viscosity and the consistency constant (Fig. 2*b* and Table 1). This is a consequence of the fact that coagulation bonds formed exclude a direct contact between the solid phase particles, which decreases inner friction in the disperse system.

The increased fluidity of molding mixtures increases the velocity of plastic deformations, which is manifested in growing plasticity (Table 1). Moreover, the high lability of the system leads to the fact that much less time is needed for transformation of elastic deformations into plastic deformation, which is evidenced by a decreased relaxation period.

The joint MCA of alumina and paraffin produces more significant modifications of the structural-mechanical and flow properties of molding mixtures. This is a consequence not only of increased chemical activity of alumina as a result of its activation. In our opinion, an important role in the formation of a coagulation structure is played by the method of introducing the surfactant. In one case alumina is dispersed without a surfactant and later nitric acid solution and paraffin are added to it. Since paraffin is a rather inert chemical com-

TABLE 1

Sample*	MCA duration, min	Alumina properties: mean particle radius, μm	coordination number	mean quadratic microdeformation, %	chemical activity,** %	Samples based on alumina – 5% paraffin – nitride acid system. Structural-mechanical characteristics: plasticity, 10^{-6} sec^{-1}	elasticity, units	relaxation period, sec	Flow properties: total flow power, MW/m^3	power on destruction of coagulation structure, MW/m^3	consistency constant, Pa · sec	flow index
						Activation without paraffin						
1	0	33	9	0.18	3.1	0.1	0.5	9000	4.2	1.9	557	0.55
2	15	12	11	0.31	5.6	0.1	0.6	7900	18.7	7.3	125	0.41
3	30	14	11	0.36	7.2	0.2	0.6	6900	21.1	8.4	123	0.39
4	45	14	12	0.40	9.3	0.3	0.6	4900	27.8	10.5	120	0.38
5	30	15	12	0.42	10.4	0.4	0.6	2800	31.6	12.8	118	0.37
						Activation in presence of paraffin						
6	15	13	12	0.38	9.6	0.1	0.6	6600	31.2	17.6	127	0.36
7	30	13	12	0.45	13.2	0.4	0.6	2200	18.8	18.8	127	0.34
8	45	14	11	0.56	14.3	0.6	0.6	1500	21.2	21.2	126	0.31
9	60	15	11	0.84	15.7	0.6	0.8	700	41.1	24.9	125	0.29

* Sample numbers correspond to numbers in Fig. 1*b*.

** Chemical activity was estimated based on the degree of dissolution of alumina in 20% nitric acid at temperature 20°C at solid : liquid = 1 : 5

pound, it is logical to assume that prevailing agents in the formation of coagulation bonds will be the peptization products (aluminum hydroxonitrates). If paraffin is activated in the presence of paraffin, mechanical sorption of the surfactant molecules on the surface takes place already at the stage of mechanical treatment in the mill. It is only later, at the mixing stage, that the hydroxonitrate binder is formed.

As for the suitability of molding mixtures for extrusion, all factors considered (increased share of plastic deformation, decreased relaxation period, increased strength of the coagulation structure, decreased flow index) are positive [2, 3]. The most effective is joint MCA of alumina and paraffin. In this case an optimum activation duration (for ring-type vibration roller mill VM-4 is lasts 50 – 60 min) [6] provides for predominant plastic deformation (45 – 55%), the required relaxation period (700 – 1500 sec), a high strength of the coagulation structure (approximately 25 MW/m^3), and the required flow index (less than 0.3). Such combination of properties makes it possible to successfully mold blocks of cellular structure from this mixture. If the purpose is to produce articles of a simple shape, the dispersion duration can be shortened by a factor of 2 – 2.5 without impairing quality.

Thus, an optimum content of paraffin in a molding mixture based on alumina peptized with nitric acid is determined, which is about 5% of dry powder weight.

Modifications of molding mixture properties depend, first, on increased chemical activity of alumina and second, on the method of introducing the paraffin additive.

Joint MCA of alumina and paraffin makes it possible to control more efficiently the structural-mechanical and flow properties of molding mixtures. This is manifested in the fact that with shorter treatment in the mill all structural-mechanical and flow parameters of the system change to a greater extent. Using joint activation of alumina and paraffin makes it possible to produce a molding mixture suitable for extrusion of blocks with a cellular structure.

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